

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
3 March 2005 (03.03.2005)

PCT

(10) International Publication Number  
**WO 2005/019934 A2**

(51) International Patent Classification<sup>7</sup>: **G03F 7/00**

(21) International Application Number:  
PCT/US2004/026701

(22) International Filing Date: 17 August 2004 (17.08.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
2003-208442 22 August 2003 (22.08.2003) JP

(71) Applicant (for all designated States except US): **3M INNOVATIVE PROPERTIES COMPANY** [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(72) Inventor; and

(75) Inventor/Applicant (for US only): **YOKOYAMA, Chikafumi** [JP/JP]; 8-8 Minami Hashimoto 3-chome, Sagami-hara, Kanagawa 229-1185 (JP).

(74) Agents: **FISCHER, Carolyn, A. et al.**; Office of Intellectual Property Counsel, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

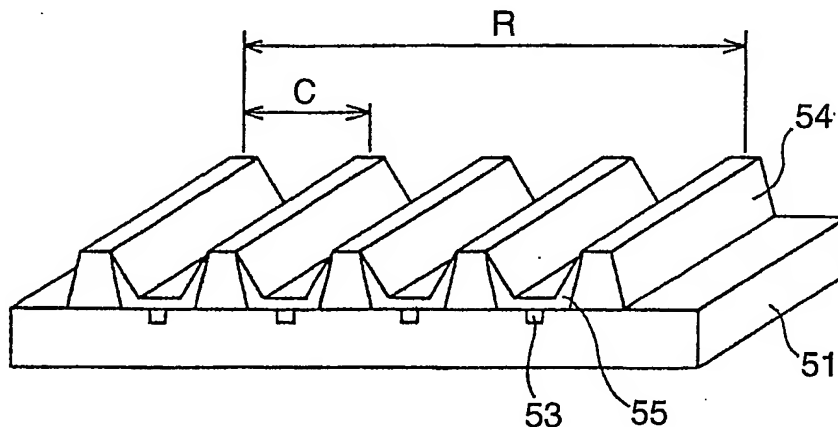
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **PRECURSOR PASTE AND METHOD OF PRODUCING THE SAME**



(57) Abstract: To provide a fine structure precursor paste that allows it to produce PDP ribs or other fine structures with high aspect ratio and high accuracy without causing pattern deformation or other defects. The photosensitive paste comprises a photosensitive material, fine ceramic particles dispersed as primary particles in the paste, and a surfactant comprising a phosphorus based compound and a sulfonate-based compound.

WO 2005/019934 A2

## **PRECURSOR PASTE AND METHOD OF PRODUCING THE SAME**

### **FIELD OF THE INVENTION**

5 The present invention relates to a photosensitive paste and, more particularly, to a precursor paste that can be advantageously used when forming a fine structure. The present invention also relates to a method of producing the fine structure by using the paste, and to the fine structure thus produced. A typical example of the fine structure is ribs formed on a back panel for a plasma display panel.

### **BACKGROUND OF THE INVENTION**

10 The flat panel displays that are small in thickness and light in weight have been gaining much attention as the next generation display apparatus. As an example of thin flat panel display of large screen, the plasma display panel (PDP) has been used for business use, and recently for home use as wall-hung television receiver.

15 The PDP has such a constitution as schematically shown in Fig. 1. While only one discharge cell 56 is shown in PDP 50 for the purpose of simplicity, the discharge cell 56 is delimited by a front glass substrate 61, a back glass substrate 51 and ribs (also referred to as barrier rib, separator or barrier wall) 54 of fine structure. The front glass substrate 61 has transparent display electrodes 63 consisting of scan electrodes and sustaining  
20 electrodes, a transparent dielectric layer 62 and a transparent protective layer 64 formed thereon. The back glass substrate 51 has address electrodes 53 and a dielectric layer 52 formed thereon. The display electrode 63 consisting of the scan electrode and the sustaining electrode, and the address electrodes 53 are perpendicular to each other and arranged at equal intervals. Each of the discharge cells 56 has a fluorescent layer 55  
25 formed on the inner wall thereof and is filled with rare gas (for example, Ne-Xe gas) so that spontaneous light emission occurs through plasma discharge between the electrodes.

In the PDP 50 described above, the rib 54 is made generally in fine structure of ceramic to which the fine structure of the present invention can be applied. Fig. 2 shows the ribs 54 of the present invention schematically as will be described in detail below, the ribs 54 being provided on the back glass substrate 51 together with the address electrodes  
30 53 so as to form the back panel of the PDP.

Since shape and dimensional accuracy of the ribs have significant influence on the

performance of the PDP, many methods have been proposed to create the ribs. One such method involves molding a precursor ceramic paste into a desired shape and then sintering the paste to create the densified ceramic ribs. Various improvements have been made on the mold and method employed for producing the same. For example, such a method of forming the ribs is proposed that a metal or glass is used as the mold material, a curable coating solution is placed between the surface of the glass substrate and the mold to form the ribs, then the mold is removed after the coating solution has been cured, and the substrate onto which the cured coating solution has been transferred is fired (See JP 9-12336). The coating solution is a paste consisting of glass powder of low melting point as a major component. This method of forming the ribs, however, has various problems such that the mold must be produced with high machining accuracy, the ribs tend to include bubbles, the ribs can easily peel off the glass substrate, and it is necessary to keep the mold and the glass substrate in close contact with each other under reduced pressure, which requires installation of a pressure reducing apparatus that adds to the producing cost and requires skilled operator.

In addition to the improvements on the mold and method employed for producing, various improvements have been made on the rib forming paste. For example, in order to enable it to form a pattern of high aspect ratio and high accuracy, there has been proposed a photosensitive paste comprising a phosphorus-containing compound, a photosensitive organic component and fine inorganic particles as essential components with emphasis on the restriction of gelation (JP 9-218509).

#### **SUMMARY OF THE INVENTION**

The present inventors have found that when rib were formed by using a flexible mold with the photosensitive paste having a viscosity of 26,000, various defects occurred due to entrapment of bubbles. The occurrence of defects due to entrapment of bubbles was particularly marked in a grid pattern.

The present inventors have found that when a surfactant comprising a phosphorus based compound and a sulfonate-based compound are mixed with a photosensitive paste, dispersibility of fine particles in the paste is improved while maintaining high content of fine ceramic particles, thereby reducing the viscosity to 20,000 cps or less.

Accordingly in one aspect, the present invention relates to a precursor paste,

comprising:

a photosensitive material;

fine ceramic particles dispersed, as primary particles, in the photosensitive material; and

5 a surfactant comprising a phosphorus based compound having at least one phosphorous atom with at least one -OH group and a sulfonate-based compound having a sulfonate group. The precursor paste preferably has a viscosity of 1,500 to 20,000 cps at 22°C.

10 In another aspect thereof, the present invention relates to a fine structure comprising a substrate and a pattern of projections of predetermined shape and dimensions formed on the surface of the substrate, that is formed by photocuring of the precursor paste of the present invention.

15 In still another aspect thereof, the present invention relates to a method of producing a fine structure comprising a substrate and a pattern of projections of predetermined shape and dimensions formed on the surface of the substrate, that comprises the steps of:

preparing a flexible mold that has a pattern of grooves of shape and dimensions, that correspond to the pattern of projections to be formed on the surface of the substrate;

20 filling the grooves of the mold with the paste such as by placing the paste in a space between the substrate and the groove pattern of the mold;

laminating the mold on the substrate;

irradiating the paste with light of predetermined wavelengths to carry out photocuring, so as to form the fine structure that comprises the substrate and the pattern of projections integrally bonded therewith; and

25 removing the mold from the fine structure.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

30 Fig. 1 is a sectional view schematically showing an example of the prior art PDP to which the present invention can be also applied.

Fig. 2 is a perspective view showing a back panel for PDP having ribs of the present invention that is an embodiment of the fine structure of the present invention.

Fig. 3 is a perspective view showing one embodiment of the flexible mold used in the present invention.

Fig. 4 is a sectional view taken along line IV-IV of the flexible mold shown in Fig. 3.

Fig. 5A-5C are sectional views sequentially showing one method of producing the back panel for PDP having ribs of the present invention.

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

The present invention is directed to a (e.g. photosensitive) ceramic paste suitable for use in the production of fine structures such as rib of PDP ribs by molding the paste based on photocuring.

The photosensitive ceramic paste includes the following three kinds of components:

- (1) a photosensitive material,
- (2) fine ceramic particles dispersed, as primary particles, in the paste, and
- (3) a surfactant comprising a phosphorus based compound having at least one phosphorous atom with at least one -OH group in the molecule and a sulfonate-based compound having a sulfonate group in the molecule. The photosensitive ceramic paste may optionally contain other additional components.

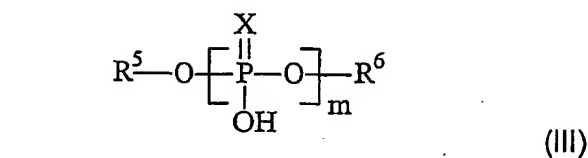
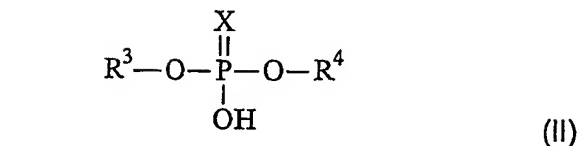
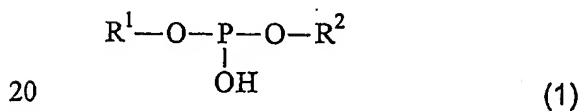
In the photosensitive ceramic paste of the present invention, a photosensitive material as a first component may be various photosensitive materials used generally in a general-purpose photosensitive paste, but is preferably a photosensitive material containing a monomer or oligomer having a (meth)acryl group in the molecule.

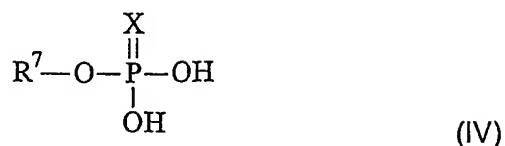
Examples of the methacryl group-containing monomer or oligomer suited for practice of the present invention include, but are not limited to triethylene glycol dimethacrylate, diethylene glycol dimethacrylate, ethylene glycol dimethacrylate, 1,6-hexanediol dimethacrylate, glycerin dimethacrylate, 2-hydroxy-3-acryloyloxypropyl methacrylate, neopentyl glycol dimethacrylate, 1,10-decanediol dimethacrylate, bisphenol A diglycidyl ether methacrylic acid adduct, and EO adduct dimethacrylate of bisphenol A. These monomer or oligomers may be used alone, or two or more kinds of them may be used in combination.

The second component, namely fine ceramic particles, include various fine ceramic particles that are commonly used for photosensitive paste. Ceramic materials that can be advantageously used in the form of fine particles in the embodiments of the present invention include, but are not limited to, glass, alumina, titania, zirconia and silica. Fine particles of these ceramic materials can be used individually or in a mixture of two or more kinds. Fine particles of one kind of ceramic material may also be covered by one or more thin coatings of another kind of ceramic material or, if necessary, by polymer coating instead of ceramic material.

While the fine ceramic particles may have various particle sizes, they have average particle size of preferably from about 0.1 to 10  $\mu\text{m}$ , and more preferably from about 0.5 to 5.0  $\mu\text{m}$ , when used in the formation of ribs or the like is taken into consideration.

Furthermore, the phosphorus based compound used as a third component (surfactant) in the photosensitive ceramic paste, together with the photosensitive resin and fine ceramic particles, is not specifically limited as far as it is a phosphorus based compound having a at least one phosphorous atom with at least one -OH group in the molecule (i.e. having at least one phosphorus-based acid group), but is preferably a phosphorus based compound represented by the following general formula (I), (II), (III) or (IV):





5 In the above formulas,

R<sup>1</sup> to R<sup>7</sup> may be the same or different and represent a hydrocarbon group having 1 to 60 carbon atoms, which may optionally contain 1 to 30 heteroatoms, such as oxygen, nitrogen, sulfur, and the like,

X represents an oxygen atom or a sulfur atom, and

10 m represents an integer of 1 to 4.

Typical examples of the phosphorus based compound include, but are not limited to, phosphorous acid monoalkyl (C1-10) esters and phosphorous acid dialkyl (C1-10) esters, such as dibutyl phosphite, butyl phosphite, dimethyl phosphite, methyl phosphite, propyl phosphite, dipropyl phosphite, diphenyl phosphite, phenyl phosphite, isopropyl phosphite, diisopropyl phosphite and n-butyl-2-ethylhexyl phosphite; phosphoric acid monoalkyl (C1-10) esters and phosphoric acid dialkyl (C1-10) esters, such as dibutyl phosphate, butyl phosphate, methyl phosphate, propyl phosphate, dipropyl phosphate, diphenyl phosphate, phenyl phosphate, isopropyl phosphate, diisopropyl phosphate and butyl-2-ethylhexyl phosphate; and thiophosphate compounds wherein oxygen of the above-mentioned phosphate esters is replaced by sulfur. Also, compounds having an unsaturated group such as acryl group, methacryl group or vinyl group at the alkyl moiety of the phosphorous acid alkyl esters may be used. Furthermore, compounds having a phosphate or phosphinate group may be used. More preferable phosphorus based compound includes a phosphorus based compound having two or more phosphate or phosphinate groups, for example, alkyl diphosphonic acid such as hydroxyethylenediphosphonic acid.

The sulfonate-based compound used, as the surfactant, in combination with the phosphorus based compound is not specifically limited as far as it is a sulfonate-based compound having a sulfonate group in the molecule, and examples thereof include:

30 sodium alkylbenzenesulfonate, calcium alkylbenzenesulfonate, sodium alkylnaphthalenesulfonate, naphthalenesulfonic acid-formalin condensate,

sodium sulfosuccinic acid dialkyl ester, sodium alkyl diphenyl ether disulfonate and the like.

For the photosensitive ceramic paste of the present invention, it is necessary to use the two kinds of compound described above in combination, as a surfactant. When these compounds are combined, a mixing ratio of the phosphorus based compound to the sulfonate-based compound (weight ratio) is usually within a range from about 99: 1 to 1: 99, and preferably from about 90: 10 to 10: 90. When the mixing ratio is out of the range described above, the fine ceramic particles cannot be dispersed to the level of primary particles, making it unable to decrease the viscosity to a desired level.

The photosensitive ceramic paste of the present invention has viscosity of 20,000 cps or less, preferably within a range from 2,000 to 10,000 cps as measured at 22°C. When the viscosity of the paste is decreased by decreasing the content of the fine glass particles in the paste, shrinkage during firing increases thus leading to inevitable problems such as increasing defects and worsening deformation of ribs. According to the present invention, a surfactant having a phosphate group is synergistically employed in combination with a surfactant having a sulfonate group. In doing so, it was unexpectedly made possible to disperse fine particles of glass or ceramic to the level of primary particles in the photosensitive paste. As a result, the viscosity could be decreased to 10,000 cps or less, for example, for a photosensitive paste containing 80% by weight of fine glass particles.

As will be described later in the appended examples, viscosity of a photosensitive paste containing 80% by weight of fine glass particles could be decreased only to a high value of 26,000 cps when only a phosphorus based compound having a phosphate group was added as a surfactant. Further, the viscosity of the photosensitive paste could be decreased only to a high value of 35,000 cps when only a sulfonate-based compound having a sulfonate group was added as a surfactant. However, in case the phosphorus based compound having a phosphate group being employed in combination with a sulfonate-based compound having a sulfonate group, as exemplified, the viscosity of the photosensitive paste could be decreased to as low as 6,000 cps. Further, the maximum particle size of the paste of the invention was about 2 to 3  $\mu\text{m}$  and fine particles of glass were dispersed as the primary particles (average particle size of about 2 to 3  $\mu\text{m}$ ), making a great contribution to the effects of the present invention.

The paste described herein was also found to have improved shelf life. For example, the paste of the invention was left to stand at 22°C for two months and found not to deteriorate as indicated by gelation.

5 The content of the fine ceramic particles in the photosensitive ceramic paste of the present invention is usually within a range from 60 to 90% by weight, and preferably from about 70 to 85% by weight. When the content of the fine ceramic particles in the paste is out of the range described above, it can adversely effect the production and characteristics of the fine structure. Adverse effects such as faulty application of the paste, damage or defect of the fine structure such as ribs and difficulty of releasing from the mold may be  
10 observed.

The photosensitive ceramic paste of the present invention optionally contains additives, which are commonly used in a general-purpose photosensitive paste, in addition to the above-mentioned components. Suitable additives include binders, photopolymerization initiators, diluents, ultraviolet absorbers, sensitizers, auxiliary  
15 sensitizers, polymerization inhibitors, plasticizers, thickeners and organic solvents.

The photosensitive ceramic paste of the present invention can have various compositions as far as it satisfies the above-mentioned constituent features, and preferably has a composition comprising:

5 to 15 parts by weight of a photosensitive resin,  
20 60 to 90 parts by weight of fine ceramic particles,  
0.1 to 1.0 parts by weight of a surfactant made of a phosphorus based compound,  
0.1 to 1.0 parts by weight of a surfactant made of a sulfonate-based compound,  
5 to 15 parts by weight of a diluent, and  
0.02 to 0.25 parts by weight of a photopolymerization initiator.

25 The ceramic paste having such a composition may contain optional additives in commonly employed amounts.

The photosensitive ceramic paste of the present invention is preferably cured by photocuring through irradiation with light via a flexible mold having a pattern of grooves of predetermined shape and dimensions being formed on the surface thereof, and is  
30 therefore useful as the fine structure-providing precursor paste. A typical example of the fine structure is ribs formed on a back panel of PDP. The pattern of grooves of the flexible mold for making the ribs on the back panel of PDP may be a straight pattern or a

plurality of grooves arranged at equal intervals substantially in parallel to each other, but is preferably a grid pattern of a plurality of grooves arranged at equal intervals substantially in parallel to each other and crossing each other. In short, the ribs of the back panel of PDP may be formed in either a straight pattern or a grid pattern, although grid pattern is preferable.

The present invention provides a fine structure having a pattern of projections of predetermined shape and dimensions formed on the surface of a substrate. The fine structure of the present invention is preferably ribs of a back panel of PDP. In the back panel of PDP, the pattern of projecting ribs may be either a straight pattern of a plurality of ribs arranged at equal intervals substantially in parallel to each other, or a grid pattern of a plurality of ribs arranged at equal intervals substantially in parallel to each other and crossing each other, but is preferably a grid pattern of ribs.

Also the present invention provides a method of producing a fine structure having a pattern of projections of predetermined shape and dimensions formed on the surface of a substrate. The method of the present invention comprises the steps of:

preparing a flexible mold that has a pattern of grooves of shape and dimensions, which correspond to the pattern of projections, formed on the surface thereof;

placing the photosensitive ceramic paste (fine structure precursor paste) of the present invention in a space between the substrate and the grooves pattern of the mold, filling the grooves of the mold with the ceramic paste and laminating the mold on the substrate;

irradiating the ceramic paste with light of predetermined wavelengths to carry out photocuring, so as to form the fine structure comprising the substrate and the pattern of projections integrally bonded therewith; and

removing the mold from the fine structure.

As described previously, the fine structure is preferably ribs of the back panel of PDP. Therefore, the method of the present invention preferably further includes the step of forming a set of address electrodes at equal intervals substantially in parallel to and independently from each other on the surface of the substrate.

The mold used in the practice of the present invention is preferably a flexible mold comprising a support and a molding layer that is provided on the support and has a pattern of grooves of predetermined shape and dimensions, which correspond to the pattern of

projection, formed on the surface thereof. The flexible mold will be described in detail later.

The practice of the present invention will be described in more detail below with reference to the accompanying drawings.

5 Fig. 2 shows ribs 54 of PDP that is a typical example of the fine structure of the present invention. The ribs 54 of PDP are formed on the back panel glass substrate 51 so as to constitute the back panel of the PDP, and can be advantageously used when incorporated in the PDP 50 as shown in Fig. 1. While the ribs 54 shown are formed in a straight pattern, a grid pattern of ribs that cross each other at right angles is also included  
10 in the scope of the present invention, and photosensitive ceramic paste of the present invention can fully achieve its excellent effects when the ribs are formed in a grid pattern.

Intervals  $c$  (cell pitch) of the ribs 54 shown in the drawing may be changed in accordance to the screen size and/or other factors, but usually within a range from about 150 to 400  $\mu\text{m}$ . Ribs are generally required to be free of defects and to have high  
15 dimensional accuracy. As to the dimensional accuracy, the ribs are required to be formed at the predetermined positions corresponding to the address electrodes with almost no deviation allowing tolerance of several tens of micrometers. A positional error of more than several tens of micrometers will have adverse effect on the condition of emitting visible light thus making satisfactory spontaneous light emission impossible. As larger  
20 screen sizes are becoming more popular, accuracy of rib pitch poses a serious problem.

When the ribs 54 are viewed as a whole, accuracy of several tens of ppm is required for the total pitch  $R$  (distance between outermost ribs: although only five ribs are shown in the drawing, actually there are about 3,000 ribs) of the ribs, while it varies a little depending on the substrate size and the rib shape. While the flexible mold comprising the  
25 support and the molding layer that is supported by the support and has a pattern of grooves is advantageously used in the practice of the present invention, accuracy of several tens of ppm is required for the total pitch  $R$  (distance between outermost grooves) of the mold, too. According to the present invention, such problems of dimensional accuracy can also be solved.

30 Although any flexible mold can advantageously be used in the practice of the present invention, the mold preferably comprises the support comprising a plastic film, and the molding layer having a pattern of grooves (groove portion) formed by molding of

a photocurable resin on one side of the support.

The support suited for practice of the present invention is a film made of a plastic material. Examples of the plastic material suited for use as the support include, but are not limited to, polyethylene terephthalate (PET), polyethylene naphthalate (PEN), stretched polypropylene, polycarbonate and triacetate. Among these plastic materials, PET film is useful as the support and, for example, polyester film such as Tetoron<sup>TM</sup> film can be advantageously used as the support. These plastic films may be used as a single-layer film, or two or more kinds of them may be used in combination as a multi-layer film.

While the plastic film may have various thicknesses depending on the constitutions of the mold and the PDP, the thickness is usually within a range from 0.01 to 1.0 mm, and preferably within a range from 0.1 to 0.4 mm. When the support has thickness out of this range, it becomes difficult to handle. Thus, a thicker support can be advantageous.

In addition to the support described above, the flexible mold has a molding layer formed thereon. As will be described in detail below, the molding layer has the pattern of grooves of predetermined shape and dimensions, which correspond to the pattern of projections such as the ribs or other fine structure of the PDP back panel to be produced by using the mold, being formed on the surface thereof and may also be called the shape forming layer. The molding layer normally consists of a single layer, but may also be formed in a multi-layer structure from two or more kinds of material having different properties if necessary. Both the support and the molding layer are preferably transparent, when it is taken into consideration that a photocurable molding material is used.

Now, the constitution of the flexible mold will be described below with reference to Figs. 3 and 4. Constitution of the ribs formed in grid pattern by photocuring using the flexible mold will also be easily understood from the following description.

Fig. 3 is a perspective view schematically showing a part of a preferable embodiment of the flexible mold, and Fig. 4 is a sectional view taken along line IV-IV of Fig. 3. As will be seen from these drawings, the flexible mold 10 is not designed for the production of the back glass substrate 51 having straight pattern of ribs comprising a plurality of ribs 54 arranged in parallel to each other shown in Fig. 2. It is for the produce of the back glass substrate having grid pattern of ribs comprising a plurality of ribs arranged substantially in parallel to each other while crossing, though not shown. The photosensitive ceramic paste of the present invention is particularly useful in producing

the back glass substrate having grid pattern of ribs.

5 The flexible mold 10 has the pattern of grooves having predetermined shape and dimensions formed on the surface thereof, as illustrated. The pattern of grooves constituted from a plurality of grooves 4 that are arranged at equal intervals substantially in parallel to each other while crossing. As such, while the flexible mold 10 can be used in the production of other fine structures, this constitution of the grooves formed on the surface in grid pattern is particularly useful in forming the PDP ribs having grid pattern of projections. The flexible mold 10 may have additional layer or the constituting layers thereof may be processed as required, but the mold is basically constituted from the support 1 and the molding layer 11 formed thereon having the groove portion 4 as shown in Fig. 3.

The molding layer 11 is preferably made of a curable material. The curable material is a thermocurable material or a photocurable material. Particularly, the photocurable material is useful because it can be cured within a comparatively short time without requiring a long and large heating furnace for formation of the molding layer. The photocurable material is preferably a photocurable monomer or oligomer, and more preferably an acrylic monomer or oligomer. The curable material can contain optional additives. Suitable additives include polymerization initiators (for example, photoinitiators) and antistatic agents.

20 Examples of the acrylic monomer suited for formation of the molding layer include, but are not limited to, urethane acrylate, polyether acrylate, acrylamide, acrylonitrile, acrylic acid and acrylate ester. Examples of the acrylic monomer suited for formation of the molding layer include, but are not limited to, urethane acrylate oligomer and epoxy acrylate oligomer. Particularly, the urethane acrylate and oligomer thereof can provide a flexible and tough cured article after curing, and can also contribute to an improvement in productivity of the mold because of very large curing rate among acrylates. Furthermore, when using these acrylic monomers or oligomers, the molding layer becomes optically transparent. Therefore, the flexible mold comprising such a molding layer enables the use of the photocurable molding material when the fine structure such as PDP ribs is produced. These acrylic monomers or oligomers may be used alone, or two or more kinds of them may be optionally used in combination.

As already mentioned, the support 1 carrying the molding layer 11 is preferably a

plastic film of which thickness is usually within a range from about 0.05 to 1.0 mm. The support is preferably optically transparent. When the support is optically transparent, since light irradiated for curing can transmit through the support, the molding layer can be formed by using a photocurable molding material. A typical example of transparent  
5 support is as described above.

When the flexible mold described above and the fine ceramic structure of the present invention are combined in the molding operation, various fine structures can be produced according to the mold and properties of the paste. For example, use of the flexible mold shown in Figs. 3 and 4 enables it to produce the ribs of PDP having grid  
10 pattern with high aspect ratio and high accuracy without requiring skills nor causing defects in the ribs. Use of the flexible mold also enables it to easily produce PDP of large screen having such a rib structure by simply using a laminate roll instead of vacuum equipment and/or a complicated process.

The present invention also provides the fine structure and the method of producing the same. While the fine structure may be formed in various structures, typical example thereof is the rib portion of the substrate (back panel) of PDP wherein the ribs are formed on a flat glass sheet. Now the method of producing the PDP substrate having the grid pattern of ribs by using the flexible mold shown in Figs. 3 and 4 will be described below with reference to Fig. 5. The producing apparatus shown in Figs. 1 to 3 of Japanese  
15 Unexamined Patent Publication (Kokai) No. 2001-191345, for example, can be advantageously used for the practice of the present invention.

Although not illustrated, a flat glass sheet having electrodes disposed thereon at equal intervals in parallel to each other is prepared in advance and is set on a surface plate. Then as shown in Fig. 5(A), the flexible mold 10 of the present invention having the pattern of grooves is placed at a predetermined position on the flat glass sheet 31, and alignment of the flat glass sheet 31 and the mold 10 is carried out. Since the mold 10 is transparent, alignment of the flat glass sheet 31 and the electrodes can be carried out easily. More specifically, the alignment is carried out either under visual observation or by using a sensor such as CCD camera so as to make the groove portion of the mold 10  
25 and electrodes on the flat glass sheet 31 parallel to each other. At this time, the mold 10 and distance between adjacent electrodes on the flat glass sheet 31 may be made equal by controlling the temperature and humidity, as required. This is because the mold 10 and the  
30

flat glass sheet 31 expand or shrink with different rates with temperature and humidity. Therefore, when alignment of the flat glass sheet 31 and the mold 10 has been completed, temperature and humidity at that time are controlled constant. Such controlling method is particularly effective for producing the PDP substrate of large surface area.

5           Then a laminate roll 23 is placed on one edge of the mold 10. The laminate roll 23 is preferably a rubber roll. The one edge of the mold 10 is preferably fixed on the flat glass sheet 31. In this way, alignment of the flat glass sheet 31 (with electrodes) and the mold 10 may be maintained during subsequent operations.

10           Then the other free edge of the mold 10 is lifted by a holder (not shown) and is moved to above the laminate roll 23 so as to expose the flat glass sheet 31. At this time, care is exercised so as not to apply tension to the mold 10, so as to prevent the mold 10 from being wrinkled and to maintain the aligned positions of the flat glass sheet 31 and the mold 10. But other means may be employed as long as the aligned positions can be maintained. With this method, since the mold 10 has elasticity, even if the mold 10 is  
15           curled up as shown in the drawing, the mold 10 returns exactly to the aligned position when laminated thereafter.

          Then a predetermined amount of the photosensitive paste 33 required to form the ribs is supplied onto the flat glass sheet 31. The photosensitive paste 33 comprises the photosensitive ceramic paste of the present invention described previously. The  
20           photosensitive ceramic paste 33 may be supplied, for example, by means of a paste hopper equipped with a nozzle.

          When applying the method shown in the drawing, the photosensitive ceramic paste 33 is supplied onto the flat glass sheet 31 not evenly over the surface. Instead, the rib precursor 33 is supplied only to a position on the flat glass sheet 31 near the laminate roll  
25           23 as shown in Fig. 5(A). This is because the photosensitive ceramic paste 33 can be spread uniformly over the flat glass sheet 31 as the laminate roll 23 moves over the mold 10 in the process to be described later. The photosensitive ceramic paste 33 has viscosity preferably within a range from 2,000 to 10,000 cps in order to carry out this operation smoothly as well. However, method of supplying the photosensitive ceramic paste is not  
30           limited to that described above. For example, the photosensitive ceramic paste may also be applied so as to coat the entire surface of the flat glass sheet, although not shown.

          Then the laminate roll 23 is moved over the mold 10 at a predetermined speed by a

motor (not shown) as indicated with an arrow in Fig. 5(A). While the laminate roll 23 is moving over the mold 10, a pressure is applied onto the mold 10 progressively from one edge to the other edge thereof by the gravity of the laminate roll 23, so as to spread the photosensitive ceramic paste 33 over the space between the flat glass sheet 31 and the mold 10 thereby filling the grooves of the mold 10 with the paste. That is, the photosensitive ceramic paste 33 fills the grooves successively while replacing the air therein. At this time, thickness of the photosensitive ceramic paste can be controlled within a range from several micrometers to several tens of micrometers by adjusting the viscosity of the ceramic paste, or the diameter, weight or traveling speed of the laminate roll.

Also according to the method shown in the drawing, the grooves of the mold also serve as channels for air flow. Even when air is captured in the grooves, the air can be efficiently purged to the outside of the mold when the pressure is applied as described above. As a result, with this method, bubbles can be prevented from remaining in the grooves even when the photosensitive ceramic paste is supplied under the atmospheric pressure. In other words, necessity to reduce the pressure can be eliminated when applying the photosensitive ceramic paste. It needs not to say that pressure may be reduced so as to make the removal of bubbles easier.

Then the photosensitive ceramic paste is cured. In case the ceramic paste 33 that is spread over the flat glass sheet 31 is photocurable, as shown in Fig. 5(B), the laminate of the flat glass sheet 31 and the mold 10 is put into a light irradiating apparatus (not shown) to irradiate the ceramic paste 33 with ultraviolet rays (UL) via the flat glass sheet 31 and the mold 10. Thus ribs are made of the photosensitive ceramic paste.

Last, the flat glass sheet 31 and the mold 10 are taken out of the light irradiating apparatus with the ribs 34 bonded onto the flat glass sheet 31, and the mold 10 is removed as shown in Fig. 5(C). The mold typically has good release properties. However, a release coating may be optionally applied to the mold to aid in easy removal of the mold 10 with less force without damaging the ribs 34 that adheres to the flat glass sheet 31. Of course, no major apparatus is required for this mold releasing operation.

EXAMPLESExample 1

Preparation of photosensitive glass paste:

- 5           To prepare a glass paste, the following materials were prepared in the following amount.

Photocurable oligomer: bisphenol A diglycidyl methacrylate acid adduct (manufactured by Kyoeisha Co., Ltd.)	318.5 g
Photocurable monomer: triethylene glycol dimethacrylate (manufactured by Wako Pure Chemical Industries, Ltd.)	136.5 g
Diluent: 1,3-butanediol (manufactured by Wako Pure Chemical Industries, Ltd.)	455.0 g
Photocuring initiator: bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (manufactured by Ciba Speciality Chemicals under the trade name of "Irgacure 819")	6.4 g
Fine ceramic particles: mixed powder of lead glass and ceramic (manufactured by Asahi Glass Co. under the trade name of "RFW-030")	4093.0 g
Phosphorus based surfactant: phosphate propoxyalkyl polyol (manufactured by 3M under the trade name of "POCA")	25.3 g
Sulfonate-based surfactant: sodium dodecylbenzenesulfonate (manufactured by Kao Co. under the trade name of "NeoPelex #25")	25.3 g

- 10           All these materials were put into an attrition mill and dispersed at 30°C for one hour with zirconia balls having diameter of 7 mm used as dispersion media.

Upon completion of the dispersing process, the paste was taken out of the attriter and was left to stand at 22°C for a whole day and night. Then viscosity of the paste was measured with a Brookfield B viscometer, with shaft #5 and rotation speed of 20 rpm employed as the measuring conditions. The paste showed viscosity of 6,000 cps.

- 15           Production of PDP back panel:

A flexible resin mold having 2593 ribs, each rib being 200  $\mu$ m in height, 100  $\mu$ m in width at the top, and 540 mm in length, at a 360  $\mu$ m pitch was made for the production of PDP back panel.

A PDP glass substrate was coated with the photosensitive ceramic paste that was

made as described above to a thickness of about 100  $\mu\text{m}$  with a coating blade. Then the flexible mold was laminated onto the glass substrate coated with the glass paste, while flexing the mold and making alignment. A laminate roll 200 mm in diameter and 100 kg in weight was moved at a speed of 40 mm per second. Pressure applied to the mold was generated only by the weight of the laminate roll.

The mold laminated onto the glass substrate was irradiated on both sides of mold and glass substrate with light having wavelengths from 400 to 450 nm for 30 seconds using an array of fluorescent lamps produced by Phillips Corp. Thus the photosensitive glass paste was cured and turned into ribs. The glass substrate with the ribs formed thereon was removed from the mold, and the glass substrate with the ribs was obtained.

Total pitch (distance between outermost ribs) was measured at five points on the mold used in the molding operation and the glass substrate that was obtained, with the results shown in Table 1.

Table 1

Measuring point	Resin mold	Rib	Difference between mold and rib
1	933.119 mm	933.112 mm	-0.007 mm
2	933.121 mm	933.117 mm	-0.004 mm
3	933.121 mm	933.122 mm	0.001 mm
4	933.121 mm	933.125 mm	0.004 mm
5	933.123 mm	933.122 mm	-0.001 mm

As will be understood from the measurement results shown in Table 1, the ribs made by using the phosphorus based surfactant and sulfonate-based surfactant in the paste according to the present invention showed dimensions almost identical with those of the mold, indicating that the ribs were formed with high dimensional accuracy.

The glass substrate with the ribs formed thereon was then fired at 550°C for one hour to remove organic components contained in the paste by combustion, thereby to form the ribs made of glass components. Upon observation of the ribs formed on the back panel with an optical microscope, no defect was detected.

Comparative Example 1

The process described in Example 1 was conducted, except for using 50.6 g of phosphorus based surfactant (phosphate propoxyalkyl polyol) instead of the combination of phosphorus based surfactant and sulfonate-based surfactant for the purpose of comparison, when making the photosensitive ceramic paste. B viscosity of the paste thus obtained was 26,000 cps (shaft #5, 20 rpm).

Then a glass substrate having ribs formed thereon was made in the process described in Example 1, using photosensitive ceramic paste prepared as described above. Since the glass paste had high viscosity of 26,000 cps in this example, greater pressure was applied when laminating the mold onto the glass substrate coated with the glass paste. Specifically, a laminate roll 200 mm in diameter and 250 kg in weight was moved at a speed of 20 mm per second. The glass substrate with the ribs formed thereon was removed from the mold, and the glass substrate having the ribs was obtained.

Total pitch (distance between outermost ribs) of the ribs was measured at five points on the mold used in the molding operation and the glass substrate that was obtained, with the results shown in Table 2.

Table 2

Measuring point	Resin mold	Rib	Difference between mold and rib
1	933.119 mm	933.114 mm	-0.005 mm
2	933.121 mm	933.136 mm	0.015 mm
3	933.121 mm	933.153 mm	0.032 mm
4	933.121 mm	933.171 mm	0.050 mm
5	933.123 mm	933.191 mm	0.068 mm

As will be understood from the measurement results shown in Table 2, the ribs made by using the paste containing only phosphorus based surfactant showed difference in dimension from the mold, about 70  $\mu$ m at the maximum. Ribs of high dimensional accuracy could not be easily formed in this example.

The glass substrate with the ribs formed thereon was then fired at 550°C for one hour to remove organic components contained in the paste by combustion, thereby to form the ribs made of glass components. Upon observation of the ribs formed on the back panel with an optical microscope, many defects were detected.

Comparative Example 2

5 The process described in Example 1 was conducted, except for using 50.6 g of sulfonate-based surfactant (sodium dodecylbenzenesulfonate) instead of the combination of phosphorus based surfactant and sulfonate-based surfactant for the purpose of comparison, when making the photosensitive ceramic paste. B viscosity of the paste thus obtained was 35,000 cps (shaft #5, 20 rpm).

10 Then a glass substrate having ribs formed thereon was made in the process described in Example 1, using the photosensitive ceramic paste prepared as described above. Since the glass paste had high viscosity of 35,000 cps in this example, greater pressure was applied when laminating the mold onto the glass substrate coated with the glass paste. Specifically, a laminate roll 200 mm in diameter and 250 kg in weight was moved at a speed of 10 mm per second. The glass substrate with the ribs formed thereon was removed from the mold, and the glass substrate having the ribs was obtained.

15 Total pitch (distance between outermost ribs) of the ribs was measured at five points on the mold used in the molding operation and the glass substrate that was obtained. Similar to Comparative Example 1, the measurements showed that the ribs had difference in dimension from the mold, about 100  $\mu\text{m}$  at the maximum. To sum up, ribs of high dimensional accuracy could not be formed in this example.

20 The glass substrate with the ribs formed thereon was then fired at 550°C for one hour to remove organic components contained in the paste by combustion, thereby to form the ribs made of glass components. Upon observation of the ribs formed on the back panel with an optical microscope, many defects were detected.

25

**What is claimed is:**

1. A precursor paste, comprising:  
a photosensitive material;  
5 ceramic particles dispersed in the photosensitive material;  
a first surfactant comprising a phosphorus based compound having at least one  
phosphorous atom with at least one -OH group; and  
a second surfactant comprising a sulfonate-based compound having a sulfonate  
group.  
10
2. The precursor paste of claim 1 wherein the paste has a viscosity of 1,500 to 20,000  
cps at 22°C.
3. The precursor paste according to claim 1, wherein the ceramic particles are present  
15 in an amount ranging from 60% to 90% by weight.
4. The precursor paste according to claim 1 or 2, wherein the photosensitive material  
comprises a monomer or oligomer having a (meth)acryl group.
- 20 5. The precursor paste according to any one of claims 1 to 3, wherein the ceramic  
particles comprise at least one material selected from the group consisting of glass,  
alumina, titania, zirconia, silica and mixtures thereof.
6. The precursor paste according to any one of claims 1 to 3, wherein the ceramic  
25 particles have an average particle size ranging from 0.1 to 10  $\mu\text{m}$ .
7. The precursor paste according to any one of claims 1 to 3, wherein the first  
surfactant is present in a ratio of 99:1 to 1:99 relative to the second surfactant.
- 30 8. The precursor paste according to any one of claims 1 to 3, wherein the paste  
comprises  
5 to 15 parts by weight of a photosensitive resin;

60 to 90 parts by weight of ceramic particles;

0.1 to 1.0 parts by weight of a first surfactant consisting of a phosphorus based compound;

5 0.1 to 1.0 parts by weight of a second surfactant consisting of a sulfonate-based compound;

5 to 15 parts by weight of a diluent; and

0.02 to 0.25 parts by weight of a photopolymerization initiator.

10 9. A article comprising a substrate and a pattern of projections of predetermined shape and dimensions formed on the surface of the substrate, that is formed by photocuring of the fine structure precursor paste of any one of claims 1 to 3.

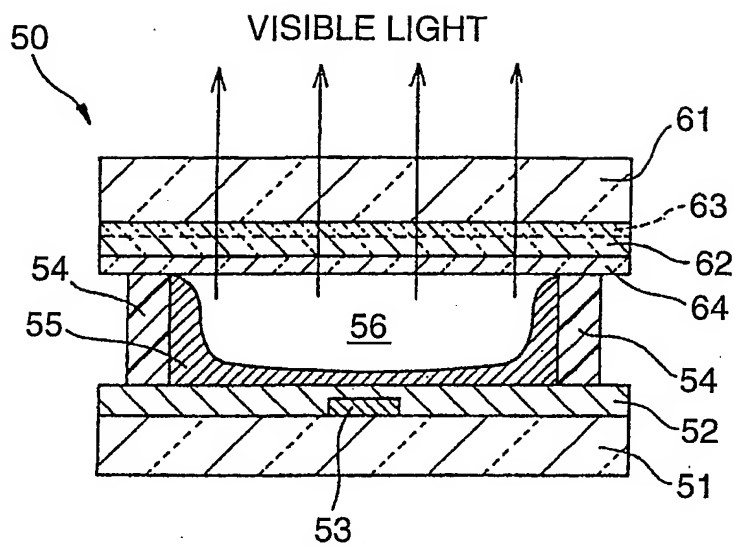
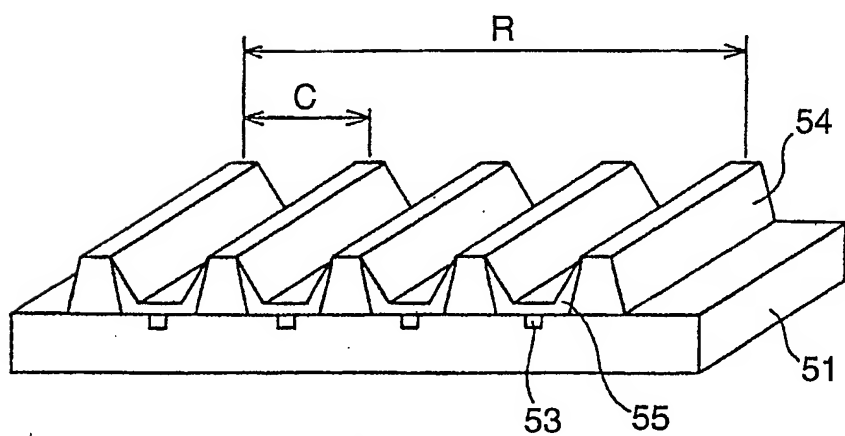
15 10. The article according to claim 9, wherein the pattern of projections is a straight pattern formed by disposing a plurality of ribs at equal intervals substantially in parallel to each other.

20 11. The article according to claim 9, wherein the pattern of projections is a grid pattern formed by disposing a plurality of ribs at equal intervals substantially parallel to each other and crossing each other.

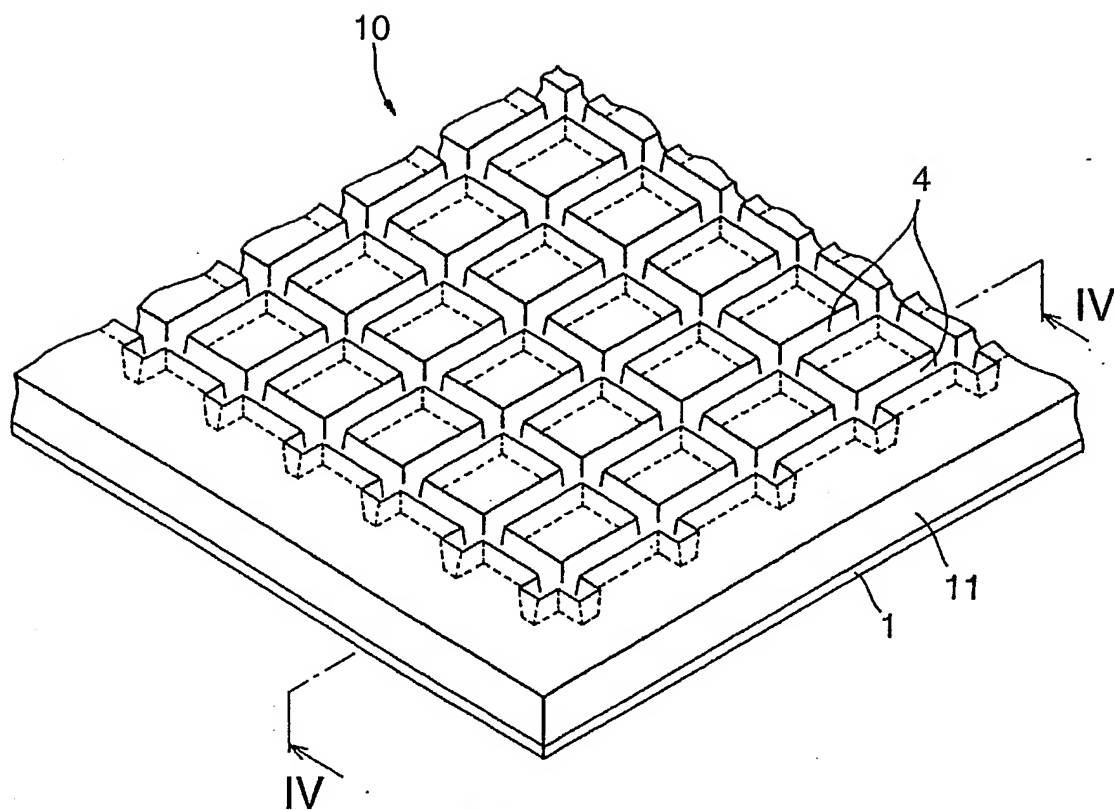
25 12. A method of producing an article comprising:  
providing a flexible mold that has a pattern of grooves of shape and dimensions that correspond to the pattern of projections to be formed;  
filling the grooves of the mold with the precursor paste of any one of claims 1 to 3;  
laminating the mold on a substrate;  
photocuring the paste; and  
removing the mold.

30 13. Plasma display panel ribs formed from the method of claim 12.

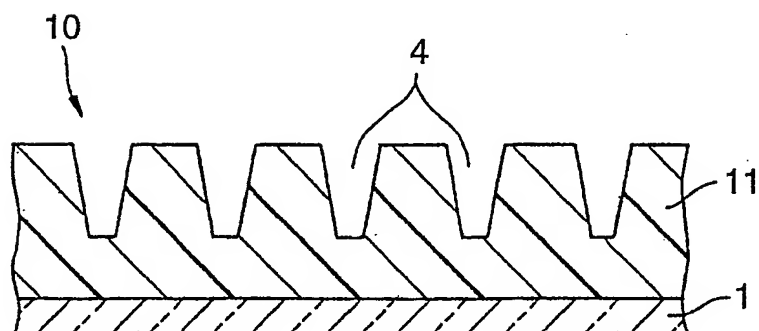
1/3

*Fig. 1**Fig. 2*

2/3

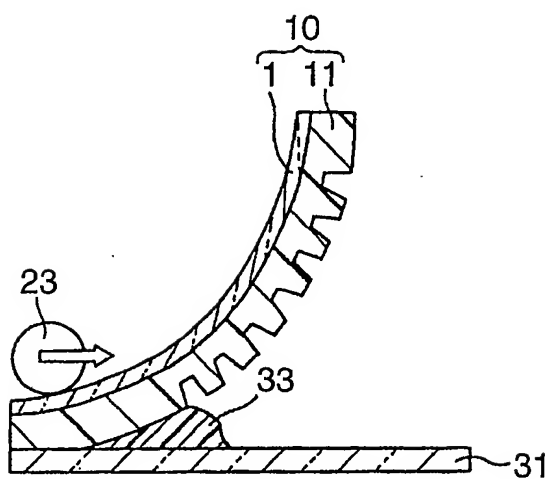
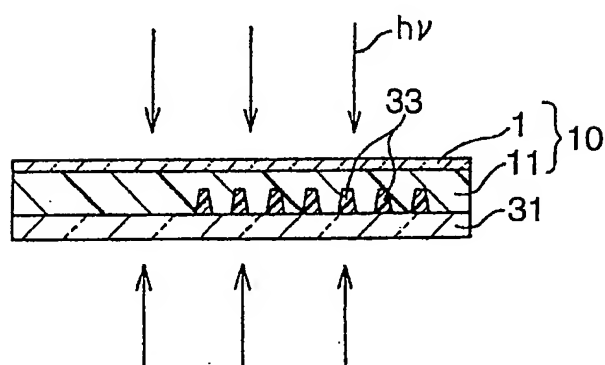
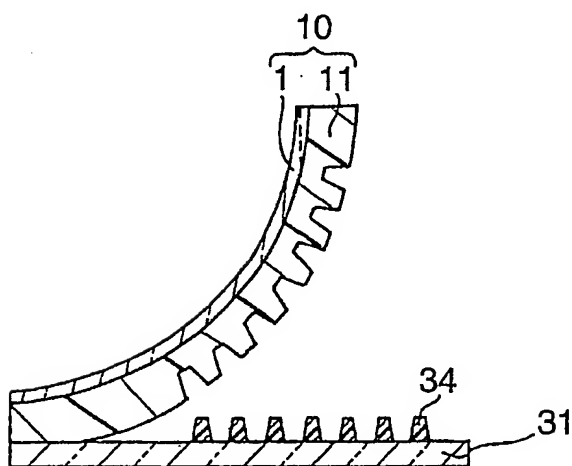


**Fig. 3**



**Fig. 4**

3/3

**Fig. 5A****Fig. 5B****Fig. 5C**